

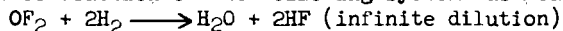
THE HEAT OF FORMATION OF OXYGEN DIFLUORIDE

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INTRODUCTION

The currently accepted value of the O-F bond energy (-45 kcal/mole) is calculated from the standard heat of formation of OF_2 (+7.6 kcal/mole) which was based on an average of three values obtained in 1930,² (5,6) the precision of which was quite poor. To determine a more reliable heat of formation of OF_2 and thus a better O-F bond energy, the heat of reaction of the following system was measured:



EXPERIMENTAL

MATERIALS

The OF_2 was obtained from the Allied Chemical Company. An assay found it to be greater than 99 percent pure. Active fluoride was analyzed by an iodometric method. By an infrared analysis 0.22 percent CO_2 and 0.02 percent CF_4 were found; SiF_4 was not detectable.

The hydrogen was a prepurified grade obtained from the Matheson Company.

APPARATUS AND PROCEDURE

The thermochemical measurements were made using a Parr fluorine combustion bomb and a Bureau of Standards calorimeter. The bomb cylinder and all internal parts of the bomb were monel. A monel ampoule was fitted into the top of the bomb to retain the OF_2 sample. The ampoule apparatus reduced the internal volume of the bomb to 315 cc. A diagram of the ampoule is given in Fig. 1 and 2.

The internal volume of the ampoule was found to be 8.7 cc. The top of the cylinder body and the cylinder head were designed with a 30-degree angular seat to accommodate a 1/2-inch monel burst diaphragm. A mechanism, which fits inside the bomb, was designed to rupture the burst diaphragm in the ampoule. This consisted of a piston with a knifelike wedge head (Fig. 3) and a small spring made from spring-tempered monel wire. The piston and spring were held in a compressed position by nickel-chromium alloy fuse wire of known calorific value, which was strung between the two internal electrodes in the bomb. A pinpoint breaker was also tried, however, because it merely punctured a small hole in the diaphragm, it increased the chance of obtaining incomplete combustion and was unsatisfactory.

The OF_2 sample was condensed in the ampoule which was then attached to the bomb head. Fifty ml of water were placed in the bomb to absorb the HF formed during reaction and thus reduce corrosion. The reaction bomb was assembled, pressurized with hydrogen (75.0 psig) and sealed. To start the reaction the sample was released into the hydrogen by electrically fusing the nickel-chromium alloy wire. This released the piston which ruptured the diaphragm and allowed the reactant gases to mix. Combustion occurred rapidly and completely; the temperature rise of the calorimeter

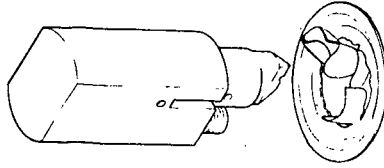


FIGURE 3

Effect of Wedge Breaking Mechanism on Rupture Disk

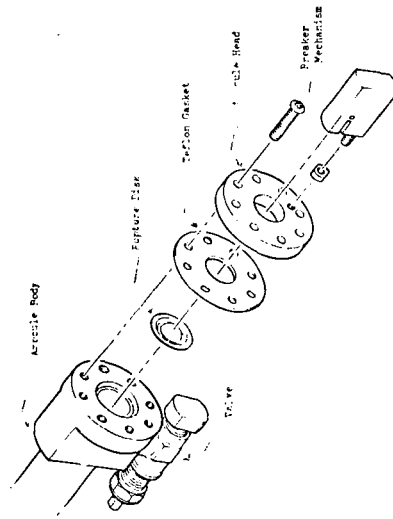


FIGURE 2

Assemble, Exploded View

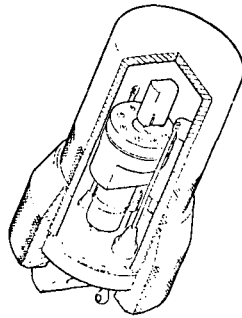


FIGURE 1

Nickel-Titanium Cocking Box with Sample Assembly

was measured by means of a platinum resistance thermometer constructed and calibrated by the Leeds and Northrup Company. The thermometer, of the four-lead cable type, was used in conjunction with a Leeds and Northrup G-2 Mueller Bridge and a high sensitivity galvanometer.

Dickinson's method was employed in order to obtain the corrected resistance change (1).

To check the mass balance of the reaction, the reaction products were analyzed after each run by a thorium nitrate method for fluoride and by a sodium hydroxide titration for hydrogen ions.

The analyses were within experimental error, but were always lower than stoichiometric for each $\text{OF}_2\text{-H}_2$ run. It was believed the approximate 5% of HF unaccounted for was consumed in the slight corrosion of the stainless-steel screw heads in the ampoule. Qualitative analysis of the screw heads did show the corroded film on the screws was the metal fluorides. The necessary thermal corrections were made on the data for this side reaction, which amounted to the formation of roughly 0.0015 mole of iron and chromium fluorides. As an additional check, a $\text{OF}_2\text{-H}_2$ run was made with the stainless-steel screws replaced by nickel-plated steel screws. No corrosion was found with the new screws and the heat of reaction agreed, within experimental error, with the results which had been corrected for the small amount of corrosion.

CALIBRATION

The energy equivalent of the calorimeter was determined by burning National Bureau of Standards Sample 39h benzoic acid. Its heat of combustion per gram under standard conditions at 25° was reported as 26,434 abs. J/g mass (weight in vacuo) with an estimated uncertainty of ± 3 J/g. This value was converted (3) to the bomb conditions used throughout this investigation and found to be 26,432.8 abs. J/g.

In a series of five calibration determinations, the mean energy equivalent for the system was 48,533.4 ± 6.5 calories/ohm.

RESULTS AND CALCULATIONS

The data are referred to a standard temperature of 25° . The energy unit used is the calorie which is defined as equal to 4.1840 absolute joules.

The quantity of heat observed during the reaction, Q , was calculated from equation (1):

$$Q = (E_s + \Delta e_2) \Delta R_c \quad (1)$$

where E_s is the energy equivalent of the calorimeter; Δe_2 is a correction for deviations from the standard calorimeter system and was computed from the heat capacities of OF_2 , H_2 , and H_2O ; and ΔR_c is the corrected temperature rise. The value of the heat capacity of OF_2 was taken as 10.35 cal/deg-mole (2).

The heat of reaction per mole in the thermodynamic standard bomb process, ΔE_R , was calculated for each experiment from equation (2):

$$-\Delta E_R = (Q - q_1 - q_2)/n \quad (2)$$

where q_1 includes corrections for nonideality of the reactant gases, condensation of water in the vapor phase, and heat of dilution of the HF solution to infinite dilution; q_2 is the energy supplied by the corrosion of the screw heads; and n is the number of moles of OF_2 . This value was reduced to the standard heat of reaction at 25°C . The calculation of ΔH_R° from ΔE_R° was done in two steps:

- a) Heats of reaction at 28°C were calculated from the energy of reaction

using the thermodynamic equation $\Delta H_R^O = \Delta F_R^O + \Delta nRT$ where Δn is the change in the number of moles of gaseous substances during reaction.

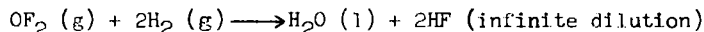
- b) Heats of reaction at 25°C were calculated from the equation $\Delta H_R^O(298.16^\circ K) = \Delta H_R^O(301.16^\circ K) + \Delta C_p(298.16-301.16)$ where ΔC_p is the difference in the heat capacity at constant pressure of the products and reactants.

The results of the experiments with OF_2-H_2 are given in Table I.

The average value of ΔH_R^O for OF_2-H_2 is 222.93 ± 0.76 kcal/mole.

DISCUSSION

Based on the measured value of the standard heat evolved from the reaction:



and combined with existing thermodynamic data (4) the calculated standard heat of formation, ΔH_R^O , of $OF_2(g)$ is -4.40 ± 0.82 kcal/mole.

The uncertainty in the heat of formation was calculated by taking the square root of sum of the squares of the precision error, the accuracy error, and the calibration error. The precision error reflects the reproducibility of the experiments and was taken as twice the standard deviation. The accuracy error was obtained by estimating the effect of the various factors on the reaction (such as purity of reactants and limits of error involved in the analyses).

The heat of formation value, combined with the most recent bond dissociation energies for fluorine and oxygen as listed in the JANAF thermochemical tables (2), yields a value of -50.8 kcal for the O-F bond energy in OF_2 .

ACKNOWLEDGMENT

We wish to acknowledge the assistance of Dr. Neal N. Ogimachi who synthesized the OF_2 used in preliminary runs and helped in loading the ampoule. The support of the research by the Air Force under contracts AF33(616)-6768 and AFO4(611)-7023 is gratefully acknowledged also.

TABLE I

DATA ON $\text{OF}_2 - \text{H}_2$ HEAT OF REACTION

Run No.	n (moles OF_2)	Δe_2 cal/ohm	ΔR_c ohm	Q cal	q_1 cal	q_2 cal	$-\Delta E_R$ kcal/mole	q_3 kcal/mole	q_4 kcal/mole	$-\Delta H_R^0$ (298.10°K) kcal/mole
1	0.023042	505.0	0.10417	5108.3	-75.7	79.2	221.54	-1.80	+0.51	222.83
2	0.023474	505.0	0.10580	5188.3	-84.1	63.4	221.91	-1.79	+0.50	223.20
3	0.025011	505.2	0.11325	5553.6	-80.9	87.1	221.80	-1.80	+0.48	223.12
4	0.024748	505.2	0.11174	5479.6	-80.4	95.0	220.83	-1.79	+0.48	222.14
5	0.023437	505.0	0.10637	5216.2	-76.9	97.9	221.67	-1.80	+0.50	222.97
6	0.014507	504.1	0.06469	3172.2	-51.5	0	222.22	-1.79	+0.70	223.31

$$\text{mean } -\Delta H_R^0 = 222.93 \pm 0.76 \text{ kcal/mole}^*$$

n is the number of moles of OF_2 ; Δe_2 is the correction for deviations from the standard calorimeter system; ΔR_c is the corrected temperature rise in the calorimeter; Q is the quantity of heat observed during the reaction; q_1 includes corrections for nonideality of the reactant gases, condensation of water in the vapor phase and heat of dilution of HF solution to infinite dilution; q_2 is the energy supplied by corrosion of the screw heads; $-\Delta E_R$ is the heat of reaction per mole in the thermodynamic standard bomb process; q_3 is the ΔnRT term to convert energy of reaction to heat of reaction; q_4 is the difference in the heat capacity at constant pressure of the products and reactants; and $-\Delta H_R^0$ is the standard heat of reaction at 25°C.

*uncertainty indicated is twice the standard deviation.

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